

Liquid-Phase Homogeneous Catalytic Oxidation of Gas Oil: Elucidation of Complex Chemical Transformation Network

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Abstract: An attempt has been made to elucidate the extremely complex chemical changes that take place when gas oils (middle distillates such as high speed diesel) are subjected to liquid phase homogeneous oxidative processing in the presence of the redox couple Co(III)/Co(II). For this purpose dilute solutions of gas oil in wet acetic acid have been treated with air under carefully controlled conditions of temperature, pressure and air flow rate. Reaction products are extracted in chloroform from an ice cold aqueous solution of the reaction mixture. Both instrumental (FTIR) and kinetic analyses endorse each other and thereby prove the sequential nature of the reaction resulting in the formation of diverse products through decomposition of the intermediate hydroperoxides, which are unstable in the presence of the catalytic redox couple Co(III)/Co(II).

Keywords: Oxidation, Homogeneous catalysis, gas oils, middle distillates, hydrocarbons, hydroperoxides.

1. INTRODUCTION

Hydrocarbons are the main constituents of crude oil, oil sands, coal, and natural gas and catalysis is undoubtedly the most important tool for selective conversion of these feedstocks into commercial chemicals of great importance. Pure hydrocarbons, isolated during refining of naturally occurring hydrocarbon stocks are conventionally employed as substrates [1]. In addition to that there are numerous examples of processes where complex hydrocarbon mixtures are used as substrates. For example coal [2-5], bitumen/asphalt/tar [6-10], wax [11], and middle distillates [12-19] have been shown to be catalytically processed either to upgrade or to desulfurize these complex mixtures.

Homogeneous catalytic oxidation forms the basis for a variety of these processes [20-27]. Especially liquid-phase processes are usually highly selective and offer a number of important advantages over their heterogeneous counterparts. In general liquid phase processes employ mild conditions and hence are particularly suitable for the application of fragile homogeneous transition metal complexes as catalysts [23, 28].

One novel preparation of the redox couple Co(III)/Co(II), had earlier been indicated as a potential homogeneous catalyst for a route from hydrocarbons (a narrow saturate cut of gas oil) to hydroperoxides that

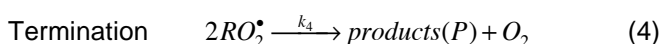
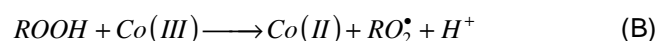
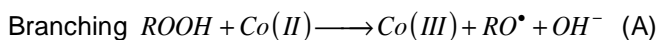
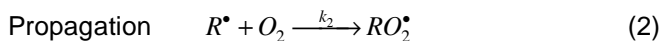
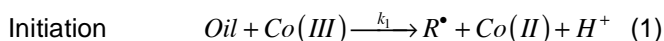
are important constituents for polymerization and oxidation processes [17, 19]. The present work was focused to establish the approximate product distribution during the homogeneous liquid phase reaction, between oxygen and a narrow saturate cut of gas oil the presence of the redox couple Co(III)/Co(II) in a medium comprising of wet acetic acid, as described earlier [17, 19]. FTIR analyses of substrate and products were used to detect the chemical changes in the time domain. The comparative FTIR spectra clearly reveal the sequential nature of changes occurring during the course of reaction. As a matter of fact FTIR analyses strongly support the kinetic predictions of the product distribution in the time domain.

2. KINETIC ANALYSIS

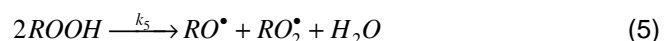
Liquid-phase oxidation of hydrocarbons is a free-radical chain reaction that is associated with long induction period due to slow initiation even at high temperature [24]. However, at low to moderate temperature the reaction can be hasten by the use of Co(II) or Co(III) ions that catalyze the decomposition of hydroperoxides, which have either been added as initiator or formed in situ [20-22, 24, 25, 29], and thereby provide a source of free radicals for propagation. Apart from this catalytic effect another notable function of Co(III) is the instantaneous initiation, even in the absolute absence of hydroperoxides. This is a manifestation of the powerful oxidizing ability of Co(III) that can abstract hydrogen from C-H bonds through direct electron transfer [17, 19, 30-32]. Based on these properties the following

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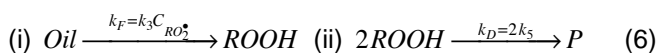
mechanism had earlier been proposed for liquid-phase air oxidation of hydrocarbon mixtures in the presence of the redox couple Co(III)/Co(II) and at sufficiently high dissolved oxygen concentration [17, 19]:



Net effect of the branching reactions (A) and (B), responsible for the catalytic effect of the redox couple Co(III)/Co(II), can be expressed by a bimolecular process that does not involve metal ions [17, 19]:



Therefore the entire process consists of the conversion of oil to hydroperoxides which are subsequently decomposed to free radicals for propagation. The path to carbonyls consists of C-C bond cleavages in some of these free radicals that can easily be oxidized further to acids [21, 22]. A rare irreversible consecutive reaction network had previously been proposed, to describe the observed kinetics of such a complex oxidation system, involving hundreds of elementary reactions, consisting of the following two simple steps [17, 19]:



According to this reaction network the rate of consumption of oil, the rate of accumulation of total hydroperoxides and the rate of production of final products may be expressed as [17, 19]:

$$\frac{dC_{\text{Oil}}}{dt} = -k_F C_{\text{Oil}} \quad (7)$$

$$\frac{dC_{\text{ROOH}}}{dt} = k_F C_{\text{Oil}} - k_D C_{\text{ROOH}}^2 \quad (8)$$

$$\frac{dC_P}{dt} = k_D C_{\text{ROOH}}^2 \quad (9)$$

The solution to differential equations (7), (8) and (9) had formerly been described [17, 19].

$$C_{\text{Oil}} = C_{\text{Oil}_0} \tau \quad (10)$$

$$C_{\text{ROOH}} = C_{\text{Oil}_0} \left[-\sqrt{\frac{\tau}{\kappa}} \left\{ \frac{I_1(\psi) - 2\beta K_1(\psi)}{I_0(\psi) + 2\beta K_0(\psi)} \right\} \right] \quad (11)$$

$$C_P = C_{\text{Oil}_0} - C_{\text{Oil}} - C_{\text{ROOH}} = C_{\text{Oil}_0} \left[1 - \tau + \sqrt{\frac{\tau}{\kappa}} \left\{ \frac{I_1(\psi) - 2\beta K_1(\psi)}{I_0(\psi) + 2\beta K_0(\psi)} \right\} \right] \quad (12)$$

Where C_{Oil_0} is the initial concentration of oil in the reaction mixture, $\tau = e^{-k_F t}$, $\kappa = C_{\text{Oil}_0} (k_D/k_F)$, $\psi = 2\sqrt{\kappa\tau}$, $\beta = I_1(2\sqrt{\kappa})/2K_1(2\sqrt{\kappa})$ and I_α and K_α are Modified Bessel Functions. The fraction of oil unreacted χ_{Oil} , the yield of hydroperoxides Y_{ROOH} and the yield of final product Y_P may be defined as:

$$\chi_{\text{Oil}} = C_{\text{Oil}}/C_{\text{Oil}_0} \quad Y_{\text{ROOH}} = C_{\text{ROOH}}/C_{\text{Oil}_0} \quad Y_P = C_P/C_{\text{Oil}_0}$$

Equations (10), (11) and (12) may thus be expressed differently, in terms of these dimensionless quantities, as:

$$\chi_{\text{Oil}} = \tau \quad (13)$$

$$Y_{\text{ROOH}} = -\sqrt{\frac{\tau}{\kappa}} \left\{ \frac{I_1(\psi) - 2\beta K_1(\psi)}{I_0(\psi) + 2\beta K_0(\psi)} \right\} \quad (14)$$

$$Y_P = 1 - \chi_{\text{Oil}} - Y_{\text{ROOH}} \quad (15)$$

Further the overall selectivity to hydroperoxides may be defined as [33]:

$$S_o = Y_{\text{ROOH}}/Y_P \quad (16)$$

3. EXPERIMENTAL SECTION

Chemical reagents, safety considerations, experimental rig and procedure for the oxidation of substrate, isolated from high speed diesel (HSD) through a complex series of steps, were described elsewhere [17, 19]. After air bubbling, the reaction mixture was diluted with an equal volume of ice cold water. Oily portion was extracted in extra pure chloroform. Extract was washed thrice with ice cold water, treated with anhydrous sodium sulphate and filtered. The filtrate was left at room temperature for complete evaporation. The FTIR spectra of substrate and processed oils were recorded on Thermo Nicolet AVATAR 319 FTIR spectrophotometer equipped with a zinc selenide attenuated total reflectance (ATR) cell.

4. RESULTS AND DISCUSSION

Categorically the substrate during the present study was an extremely complex mixture of saturates (paraffins + some naphthenes) as the chief constituents. Although some monoaromatics were present, the oil was virtually free from olefins and hydroperoxides [17, 19]. Consequently the hydroperoxides obtained during air oxidation of the substrate would be saturated hydroperoxides.

Moreover oxidative treatment is expected to result in a further complex system comprising of the full spectrum of unreacted hydrocarbons and oxygenates. Therefore establishment of exact product distribution is extremely difficult, though not impossible, even with the help of most modern analytical techniques. Nevertheless, analytical techniques such as FTIR, is at least capable of resolving such complex mixtures into various compound types.

4.1. Qualitative Chemical Transformation Network

Comparative FTIR profiles of substrate and processed oils (Figure 1) clearly reflect features related to the oxidative changes. The profiles undoubtedly

show an extremely complex change in the chemistry that occurs during the oxidative treatment in the presence of the redox couple Co(III)/Co(II). Four main compound types originate as the result of oxidative processing under described conditions. These include hydroperoxides ($3700\text{--}3300\text{ cm}^{-1}$), carbonyls ($1760\text{--}1710\text{ cm}^{-1}$), acids ($3300\text{--}2500$, $1750\text{--}1680$, $1300\text{--}1190$, and $950\text{--}900\text{ cm}^{-1}$), and olefins ($3019\text{--}3000$, and $990\text{--}940\text{ cm}^{-1}$). The intensity of IR bands for these compounds has a rising trend with the increase in air bubbling time. However, there is no prominent peak around 3350 cm^{-1} , so production of hydrogen bonded alcohols and phenols rules out.

Hydroperoxides are the primary products of the reaction under consideration that is established through rigorous experimental work [17, 19]. Concentration of hydroperoxides never excessively builds up in the system as these are unstable at the reaction conditions and decompose to give final products. Therefore the IR band for hydroperoxides has an extremely feeble and broad peak in the spectra for products.

Free radicals produced as a result of the decomposition of hydroperoxides undergo $C-C$ bond

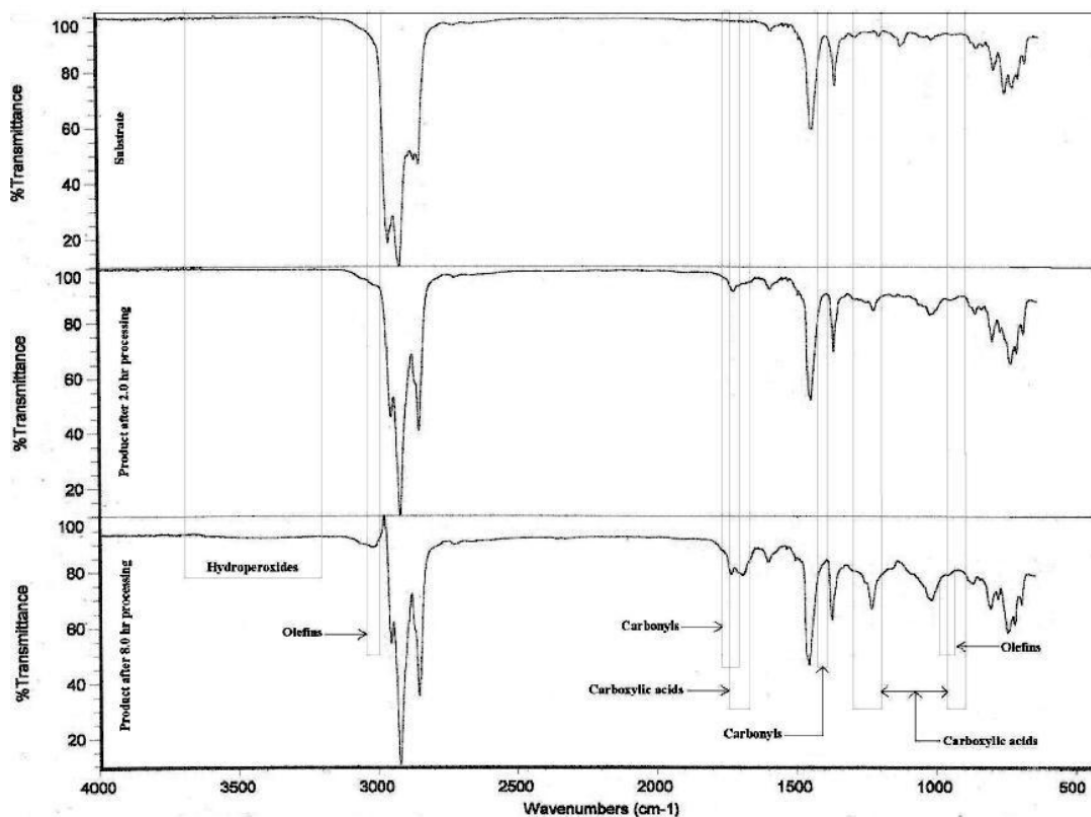


Figure 1: Comparative FTIR profiles of substrate and processed oils. Reaction conditions: $P = 50$ psig, $Q_{Air} = 1.0$ L/min, $C_{Oil_0} = 0.01795$ mol/L, $V_R = 200$ mL, $T = 55^\circ\text{C}$, $x = 0.50$, $C_{Co} = 0.005$ mol/L, $C_{H_2O} = 1.725$ mol/L, $P_{KCl} = 50\%$. [19].

cleavages leading to carbonyls that are further oxidized to corresponding acids [20-22, 25, 29]. Alcohol formation on the other hand could be possible through the following reaction [21, 22, 27]:



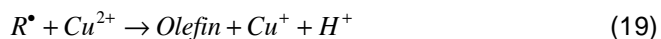
However, in acetic acid or wet acetic acid medium following cleavage is favored [34]:



This could be the most probable reason for not having any peak around 3350 cm^{-1} , indicative of the absence of H-bonded alcohols. Thus with the rise of air bubbling time the following sequence results as detected by the FTIR spectroscopy:



Trace olefin formation on the other hand may be attributed to the cleavage of alkyl radicals at the adjacent C-H bonds [20]. Another likely route to olefin formation can be described in terms of the H-abstraction capability of transition metal ions, as described for copper [35] where Cu (II) ions effectively dehydrogenate alkyl radicals yielding olefins:



A similar termination with Co (III) may be assumed, perhaps with lower probability in pressurized oxidation system ensuring plenty of dissolved oxygen for reaction 2.

4.2. Quantitative Chemical Transformation Network

The product distribution within the reactor can quantitatively be represented using the kinetic model represented by equations (13-16). These equations involve two rate constants (k_F , the rate constant for pseudo-first order formation of hydroperoxides and k_D , the rate constant for the second order decomposition of hydroperoxides). The experimentally determined values for these rate constants are given in Table 1, which have been used to construct the complex product distribution profiles for varying sets of process variables (Figure 2a and 2b).

As is evident the hydroperoxides which are the primary products of oxidation never accumulates too much within the reactor as these are unstable under the reaction conditions and in the presences of the redox couple Co(III)/Co(II). Therefore their yield profiles

Table 1: Experimentally Determined Rate Constants At Diverse Experimental Conditions [17, 19]

	$k_F \times 10^4 \text{ (s}^{-1}\text{)}$	$k_D \text{ (Lmol}^{-1}\text{s}^{-1}\text{)}$
<i>x</i>		
0.00	0.0926	12.2381
0.25	5.9238	19.8809
0.50	10.4419	8.5744
0.75	13.1680	6.5175
1.00	7.1139	0.8901
<i>C_{Co}</i> (mol/L)		
0.001	1.2785	4.8022
0.003	2.5541	9.5797
0.007	5.3632	2.7726
0.009	3.6173	1.4649
<i>C_{H₂O}</i> (mol/L)		
0.500	5.2559	6.5626
1.113	2.5856	5.0464
2.913	14.8460	23.6991
4.100	5.3478	17.6587
<i>P_{KCl}</i> (%)		
0	4.9307	9.9263
25	4.1662	11.8060
75	3.1987	8.9367
100	5.8402	13.4007
<i>T</i> (°C)		
25	2.6373	0.7332
40	3.8436	1.8611
70	1.6639	4.4346
85	1.1701	3.9097

$P = 50 \text{ psig}$, $Q_{Air} = 1.0 \text{ L/min}$, $C_{Oils} = 0.01795 \text{ mol/L}$, $V_R = 200 \text{ mL}$. Mean position for other variables were $x = 0.50$, $C_{Co} = 0.005 \text{ mol/L}$, $C_{H_2O} = 1.725 \text{ mol/L}$, $P_{KCl} = 50 \%$ and $T = 55^\circ \text{ C}$.

show an initial abrupt build up and then very shortly the subsequent decay to final products. This quantitative behavior of hydroperoxides is in excellent agreement with the qualitative FTIR profiles that show only a wide and weak signal for hydroperoxides. On the other hand the profiles for final product show a sigmoidal growth. Initially such products are not present in reactor and slowly build up as a result of the decomposition of the hydroperoxides, which is in accordance with the FTIR profiles for various durations of processing. In contrast

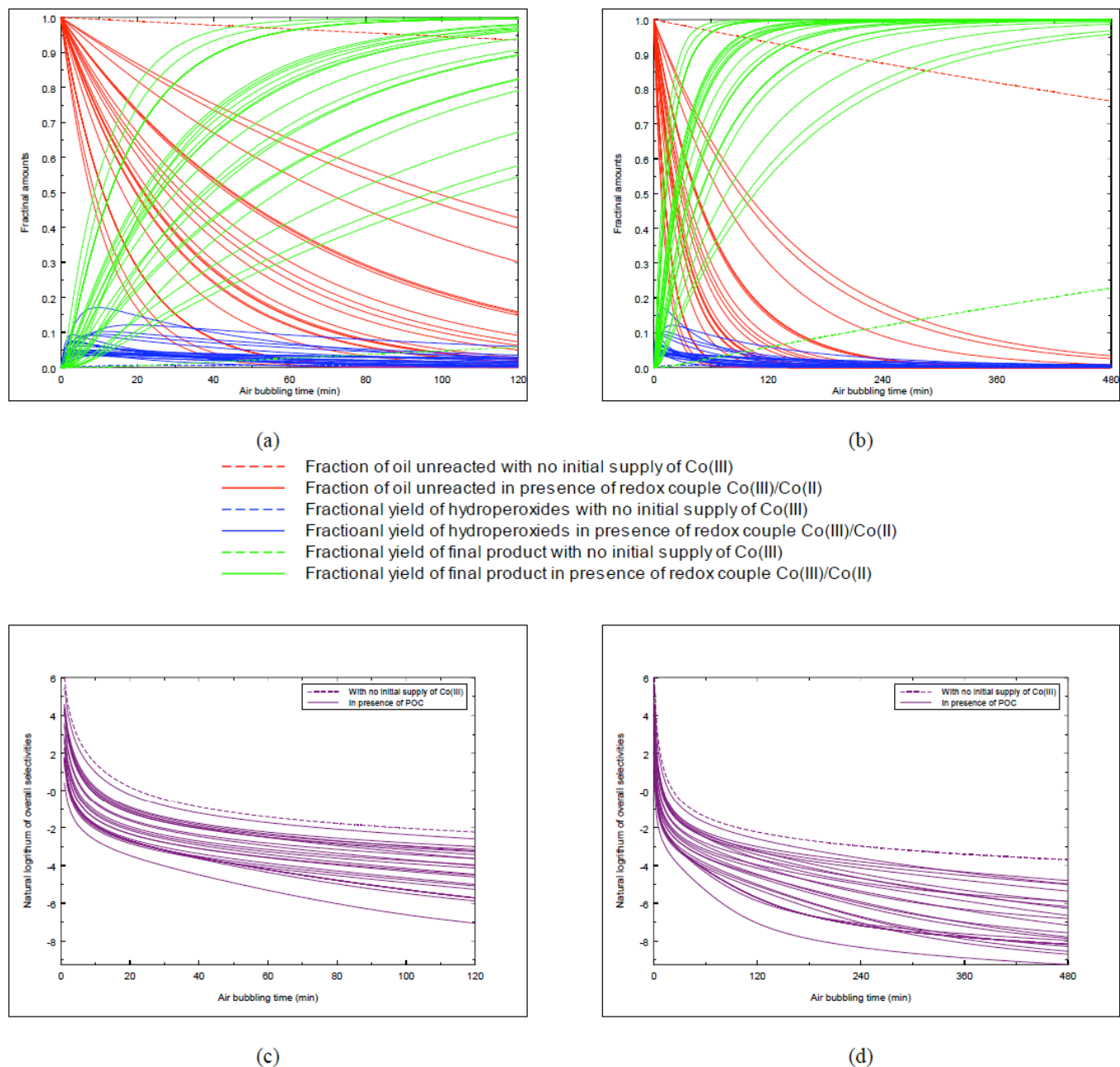


Figure 2: Kinetic predictions of conversion, yield and selectivity within the reactor during liquid-phase homogeneous catalytic air oxidation of a narrow cut of gas oil in the presence of the redox couple Co(III)/Co(II) (a) Product distributions after 2 hours of air bubbling. (b) Product distributions after 8 hours of air bubbling. (c) Overall selectivities after 2 hours of air bubbling. (d) Overall selectivities after 8 hours of air bubbling. Reaction conditions: $P = 50$ psig, $Q_{Air} = 1.0$ L/min, $C_{Oil_o} = 0.01795$ mol/L, $V_R = 200$ mL, $25 \leq T \leq 85$ °C, $0 \leq x \leq 1$, $0.001 \leq C_{Co} \leq 0.009$ mol/L, $0.5 \leq C_{H_2O} \leq 4.1$ mol/L, $0 \leq P_{KCl} \leq 100$ %.

to this the substrate follows a straightforward uninterrupted exponential decay throughout the course of reaction. The overall selectivity of hydroperoxides (Figure 2c and 2d) decreases continuously in the time domain which is again indicative of the fact that hydroperoxides are unstable intermediates and slowly decompose to final products which again supports the FTIR findings.

CONCLUSION

The reaction between hydrocarbons and air, in the presences of the redox couple Co(III)/Co(II) in wet acetic acid and in the presence of ample dissolved oxygen, results in an extremely complex product distribution. It has been precisely predicted by kinetic analyses and excellently verified by FTIR analyses that the primary products of this reaction are

hydroperoxides which are subsequently decomposed, under the influence of the catalytic nature of the redox couple Co(III)/Co(II), to a variety of oxygen containing compounds (carbonyls and acids) and to some extent olefins.

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NOMENCLATURE

- C_{Co} = Concentration of cobalt in reaction mixture, mol/L
- C_{H_2O} = Concentration of water in reaction mixture, mol/L
- P_{KCl} = Excess chloride ions in reaction mixture, %
- Q_{Air} = Flow rate of air through the reactor, L/min
- x = Fraction of Co(III) ions in the redox couple Co(III)/Co(II)
- C_{Oil_0} = Initial concentration of oil in reaction mixture, mol/L
- P = Operating pressure, psig
- T = Operating temperature, °C
- V_R = Volume of reaction mixture, mL

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